Coupled Cluster Study of the Heats of Formation of UF_6 and the Uranium Oxyhalides, UO_2X_2 (X=F, Cl, Br, I, At)

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Abstract

The atomization enthalpies of the U(VI) species UF_6 and the uranium oxyhalides UO_2X_2 (X=F, Cl, Br, I, At) were calculated using a composite relativistic Feller-Peterson-Dixon (FPD) approach based on scalar relativistic DKH3-CCSD(T) with extrapolations to the CBS limit. The inherent multideterminantal nature of the U atom was mitigated by utilizing the singly charged atomic cation in all calculations with correction back to the neutral asymptote via the accurate ionization energy of the U atom. The effects of SO coupling were recovered using full 4-component CCSD(T) with contributions due to the Gaunt Hamiltonian calculated using Dirac-Hartree-Fock. The final atomization enthalpy for UF_6 (752.2 kcal/mol) was within 2.5 kcal/mol of the experimental value, but unfortunately the latter carries a ±2.4 kcal/mol uncertainty that is predominantly due to the experimental uncertainty in the formation enthalpy of U atom. The analogous value for UO_2F_2 (607.6 kcal/mol) was in nearly exact agreement with experiment, but the latter has a stated experimental uncertainty of ±4.3 kcal/mol. The FPD atomization enthalpy for UO_2Cl_2 (540.4 kcal/mol) was within the experimental error limits of ±5.5 kcal/mol. FPD atomization energies for the non-U-containing molecules (used for reaction enthalpies) H_2O and HX (X=F, Cl, Br, I, At) were within at most 0.3 kcal/mol of their experimental values where available. The FPD atomization enthalpies, together with FPD reaction enthalpies for two different reactions, were used to determine heats of formation for all species of this work with estimated uncertainties of ±4 kcal/mol. The calculated heat of formation for UF_6 (-511.0 kcal/mol) is within 2.5 kcal/mol of the accurately-known (±0.45 kcal/mol) experimental value.

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INTRODUCTION

Molecules containing uranium are of particular importance due to their relevance to the nuclear fuel cycle, but also in regard to national security concerns. These species, however, present substantial experimental and theoretical difficulties for the quantitative determination of their thermochemical and spectroscopic properties due to the presence of multiple accessible oxidation states, partially filled 5f and 6d shells, and the vital impact of relativistic effects. To this date, there is still a severe paucity of experimental thermochemical data for gas phase actinide species that meets the general criterion of chemical accuracy, i.e., 1 kcal/mol. In particular, and of relevance to this study, only one uranium-containing molecule has an enthalpy of formation known[1] to be better than 1 kcal/mol, UF_6. Even the standard formation enthalpy of gaseous uranium atom carries an experimental uncertainty of 1.9 kcal/mol.[2] In computational studies, the most unambiguous route to the heat of formation is through the use of calculated atomization energies. These are then paired with experimental atomic enthalpies of formation, which are generally accurately known, to determine the desired molecular heat of formation. Reaction enthalpy schemes can also be used with the caveat that these generally require some number of experimentally known molecular enthalpies of formation. In either case, the calculation of an atomization or reaction enthalpy that achieves or approaches chemical accuracy by quantum chemical methods in all practical cases, even for elements much lighter than actinides, requires a composite approach, i.e., recovering as much of the required physics as possible in a series of systematic calculations, rather than in a single, very large, intractable calculation. Over the last few years, we have been modifying the Feller-Peterson-Dixon (FPD) composite approach[3,4] to address the accurate calculation of the thermochemical properties of actinide-containing molecules. By accounting for correlation effects via the coupled cluster method, inclusion of outer-core correlation, scalar relativity from the outset, and spin-orbit coupling using 2-component or 4-component correlated methods, bond dissociation enthalpies have been obtained that in some instances have rivaled the best experimental values, primarily for Th-containing molecules,[5-9] but also recently including small uranium-containing species.[10-12]

In the present study, in addition to the atomization enthalpy of the UF_6 molecule, which provides an important benchmark of the method, the entire sequence of uranium oxyhalide molecules, UO_2X_2 from X=F to At, are subjected to the same methodology. To complement the calculation of formation enthalpies via the atomization energy route, two different reaction enthalpies have also been employed - one involving UF_6 and the other UO_2F_2. Both rely on the accurate experimental enthalpies for molecules such as H_2O and HX (X=F-I). The resulting FPD atomization enthalpies are expected to be accurate to at least 3 kcal/mol while the resulting formation enthalpies have larger uncertainties due to the experimental uncertainties of the underlying atomic and molecular species that were employed.

COMPUTATIONAL DETAILS

Equilibrium geometries and harmonic vibrational frequencies were calculated at the singles and doubles coupled cluster with perturbative triples [CCSD(T)] level of theory[13,14] using triple-zeta basis sets. The cc-pVTZ-PP set was used for U,[15] aug-cc-pVTZ-PP for Br, I, and At,[16,17] while aug-cc-pVTZ and aug-cc-pV(T+*d*)Z were used for H/O/F and Cl, respectively.[18-20] The -PP sets utilized energy consistent, small-core relativistic pseudopotentials that replaced 10, 28, and 60 electrons for Br, I, and At/U, respectively.[16,21] All molecules possess closed shell singlet ground states. Only valence electrons were correlated, which is defined by the 6s6p6d7s5f electrons of U, 2s2p for O/F, 3s3p for Cl, 4s4p for Br, 5s5p for I, and 6s6p for At. The resulting equilibrium structures were used as reference geometries for all further calculations in this work. The calculated geometries and harmonic frequencies can be found in Tables S1 and S2, respectively, of the Supplemental Information. The harmonic frequencies at this level of theory for UF_6 were taken from Ref. [22].

The relativistic Feller-Peterson-Dixon (FPD) composite thermochemistry approach[3,4,15] was used to determine accurate relative energetics for all molecules, defined in this work as:

$$\mathrm{E_{FPD}} = \mathrm{E_{VQZ-DK}} + \delta\mathrm{E_{CBS}} + \delta\mathrm{E_{CV/CBS}} + \delta\mathrm{E}_{SO} + \delta\mathrm{E_{Gaunt}} + \delta\mathrm{E_{QED}} + \mathrm{E_{ZPE}} \quad (1)$$

The majority of these calculations used the third-order Douglas–Kroll–Hess (DKH3) scalar relativistic Hamiltonian[23-25] with all-electron DK-contracted basis sets. For valence correlation these corresponded to cc-pVnZ-DK3 for U,[15,26] aug-cc-pVnZ-DK for H, O, F, Br, and I,[19,20,27-29] aug-cc-pV(n+*d*)Z for Cl,[18] and aug-cc-pVnZ-DK3 for At (n=T, Q).[27] These will be denoted as VnZ-DK below. Calculations with outer-core electrons correlated, i.e., 1s for O and F, 2s2p for Cl, 3s3p3d for Br, 4s4p4d for I, and 5s5p5d for At and U utilized the analogous sets extended for core-valence correlation,[30] i.e., aug-cc-pwCVnZ-DK for O through I and aug-cc-pwCVnZ-DK3 for At and U. These are subsequently denoted as wCVnZ-DK. The atomic calculations utilized restricted open-shell HF (ROHF) orbitals, and the open-shell CCSD(T) allowed for some spin relaxation in the CCSD calculations, i.e., the R/UCCSD(T) method.[31,32]

The first term in Eq. (1), $E_{VQZ\text{-}DK}$, represents the total energy calculated with correlation of only the valence electrons at the CCSD(T) level of theory with the VQZ-DK basis sets. Complete basis set extrapolations with n=T and Q results were performed in order to determine δE_{CBS}, which is defined as $E_{CBS} - E_{VQZ\text{-}DK}$ with only valence electrons correlated. The CBS limits for the HF and correlation energies were calculated separately using the wCVnZ-DK basis sets. The Hartree-Fock CBS limits were extrapolated using[33]

$$E_n^{HF} = E_{CBS}^{HF} + A(n+1)e^{-6.57\sqrt{n}}\ , \tag{2}$$

while the correlation energies were extrapolated with[34,35]

$$E_n^{Corr} = E_{CBS}^{Corr} + B\left(n+\frac{1}{2}\right)^{-4}, \tag{3}$$

where in both cases n=3 (TZ) and 4 (QZ). The sum of these two CBS limits yields the total E_{CBS}.

$\delta E_{CV/CBS}$ represents the contribution from correlation of the outer-core using wCVnZ-DK basis sets, extrapolated to the CBS limit using Eq. (3). These core-valence contributions were calculated as the difference between the CCSD(T) energy from correlation of the outer-core electrons with the valence electrons and the energy from correlation of only the valence electrons.

The effects from spin-orbit coupling (SO) were accounted for by using the combination of two separate contributions, δE_{SO} and δE_{Gaunt}, using 4-component (4c) methods. Each of these was computed using uncontracted double-zeta basis sets of Dyall[36], v2z on U with their diffuse-augmented versions, av2z for all other elements.[37-39] The ΔE_{SO} term was calculated using full four-component, valence-correlated CCSD(T)[40] as the difference in energy between calculations using the Dirac-Coulomb (DC) Hamiltonian and analogous calculations using Dyall's spin-free Hamiltonian.[41] In these calculations a finite nuclear model (Gaussian charge distribution) was used[42] with virtual orbital cutoffs of 13 a.u., and the replacement of the (SS|SS) (small component) type Coulomb integrals by an interatomic SS correction.[43] ΔE_{Gaunt} represents the energy contribution from the Gaunt term of the Breit Hamiltonian (containing the spin-other-orbit term). These calculations were completed at the Dirac Hartree-Fock (DHF) level of theory as the difference in energy between calculations with the DC-Gaunt (DCG) and DC Hamiltonians. In the case of the open-shell atoms, the average-of-configuration (AoC) DHF method was used by distributing the open-shell electrons in just the outermost spinors (*p*-type for O and the halogens, 5f7s for U). Due to difficulties utilizing 4c-CCSD(T) on the O atom, the *J*-average of the experimental SO energy levels[44] were used for ΔE_{SO} in that case.

Accurate calculation of the atomization energies of uranium-containing molecules at the CCSD(T) level of theory is complicated by the strong multideterminantal nature of the ground state of the U atom. This was mitigated in this work by referencing all energy differences to the U^+ atomic cation, which has a $7s^2 5f^3$ (^4I) electronic ground state, which is much more amenable to accurate calculation by (scalar relativistic) CCSD(T). The final energetics were then corrected to the correct neutral asymptote by use of the accurately known experimental ionization energy of the U atom, 142.838(1) kcal/mol.[45,46] This is similar in approach to our previous work on Th-containing molecular cations where in those cases the ground state of Th^+ is problematic for CCSD(T).[5] Furthermore, with spin-orbit included in the Hamiltonian, the U^+ ground state was too multideterminantal for reliable use of 4c-CCSD(T), so correlation effects on ΔE_{SO} were recovered by using the difference between Kramers-restricted configuration interaction (KRCI)[47-49] and spin-free multireference CI (MRCI).[50] A valence AoC-DHF active space was used for these calculations and all single and double excitations were taken into the virtual space with a virtual orbital cutoff of 15 a.u.

The effects from quantum electrodynamics, $\delta E_{QED,}$ represents the energy contribution from the Lamb shift. These include the vacuum polarization, which is described by a Gaussian fit[15] to the Uehling potential, and self-energy contributions taken from the work of Pyykkö and Zhao[51]:

$$V_{SE} + V_{VP} = Be^{-\beta r^2} - \frac{1}{r} \sum b_i e^{-\alpha_i r^2} \tag{4}$$

This local potential was included in the 1-electron DK Hamiltonian for all elements except H, F, and Cl. The wCVTZ-DK basis sets were used throughout in valence-correlated CCSD(T) calculations for this contribution.

Finally, E_{ZPE} represents the zero-point vibrational energy contribution, which utilized the CCSD(T)/VTZ-PP harmonic frequencies described above. Thermal corrections to the enthalpies from 0 to 298 K, denoted dH(298) below, were calculated using standard expressions from harmonic oscillator-rigid rotor gas-phase partition functions. The MOLPRO *ab initio* suite of programs[52,53] was used for all calculations in this work except for those involving spin-orbit coupling, which were calculated via the DIRAC program.[54,55]

Heats of formation for the uranium oxyhalides (except for UO_2At_2) were calculated in two ways, (a) from the FPD atomization energies utilizing the experimental formation enthalpies of the atoms and (b) from the FPD-calculated reaction enthalpies at 298 K for

$$UF_6 + 2H_2O + 2HX \rightarrow UO_2X_2 + 6HF \qquad (5)$$

and

$$UO_2F_2 + 2HX \rightarrow UO_2X_2 + 2HF \qquad (6)$$

where the experimental 298 K formation enthalpies of UF_6, UO_2F_2, H_2O, and HX (X=F, Cl, Br, and I) were utilized. Accurate experimental values for water and the hydrogen halides were taken from the Active Thermochemical Tables (ATcT),[56-58] while those for UF_6 (-513.53 ± 0.45 kcal/mol) and UO_2F_2 (-323.3 ± 2.4 kcal/mol) were obtained from the compilation of Guillaumont et al.[1] The CODATA value for the formation enthalpy for U atom was adopted (127.4 ± 1.9 kcal/mol)[2,59] and the remaining atomic enthalpies of formation were obtained from the ATcT.[56] Unfortunately, experimental formation enthalpies for atomic At and HAt were not available. All the values used in this work can be found in Table S3 of the Supplemental Information.

RESULTS AND DISCUSSION

As is well known, the C_{2v} structures of UO_2X_2 consist of a near-linear UO_2 moiety with UO_2^{2+} bonding characteristics with a much more open X-U-X bond angle, see Figure 1 The calculated CCSD(T)/VTZ-PP equilibrium geometry parameters are given in Table S1, where it can be seen that the O-U-O angle only slightly decreases from 169º for X=F to 164º in UO_2I_2. Likewise, the X-U-X angle also decreases with increasing halogen size, ranging from about 114º in UO_2F_2 to 106º in UO_2I_2. As expected, as X ranges from F to At, the U-X distance significantly lengthens while R_{UO} changes only slightly. The equilibrium U-F bond length in UO_2F_2 is longer by about 0.08 Å than that in UF_6. The U-O bond slightly decreases from X=F to At. A similar trend calculated for the analogous anions[60] was previously attributed to an increase in covalency in these uranyl bonds. The present equilibrium geometries are in qualitative agreement with the previous DFT results of Kovács and Konings[61] who investigated the uranium oxyhalides from F to I. Their U-O bond lengths were calculated with DFT (BP86), however, these are longer than the current coupled cluster values by about 0.03 Å and the X-U-X angles are smaller by as much as 9º. The present equilibrium geometry for UO_2F_2 is nearly identical to the previously reported CCSD(T)/VQZ-PP values[22] where the latter resulted in slightly shorter bond distances. In the previous DFT (B3LYP) study of Privalov et al.,[62] their calculated equilibrium geometry for UO_2F_2 is nearly identical to the current CCSD(T) results. Finally, the results shown in Table S1 for the equilibrium geometry of UO_2Cl_2 are nearly identical to the X2C-CCSD(T)/VTZ calculations of Marshall et al.[63] In regard to the harmonic frequencies shown in Table S2, the highest 3 frequencies exhibit very little change as X varies from F to At since those modes are almost pure UO_2 stretches or bends. As might be expected, the others decrease in magnitude as the mass of the halogen increases. The previous DFT calculations of Ref. [61] are in qualitative agreement with the CCSD(T) values of Table S2 for X=F through I, while the B3LYP values of Privalov et al.[62] are in surprisingly good agreement for UO_2F_2. In addition, the present harmonic frequencies for UO_2Cl_2 agree to within a few cm^{-1} with the X2C-CCSD(T) results of Ref. [63], although the symmetric O-U-O bending mode, as well as the twisting mode, differ by about 30 cm^{-1}.

Table 1 gives the contributions of Eq. (1) to the final FPD atomization enthalpies, ΔH_{atom}, of all the species of this work, including H_2O and HX (X=F-At) since these are utilized in the reaction enthalpy calculations. In regard to the U-containing species, it is noteworthy that the effects of both the frozen-core basis set extrapolation and outer-core correlation are very important, ranging from 5 to 7 kcal/mol. In particular, they are opposite in sign to each other such that if both were omitted for some reason, the final result might be in fortuitous agreement with the more complete treatment. The difference between the frozen-core CBS limit and the VQZ-DK result increases slightly from UO_2F_2 to UO_2Cl_2 and then slightly decreases to UO_2At_2. The effect of correlating the outer-core electrons is largest for the atomization energy of UF_6, only slightly smaller in magnitude for UO_2F_2 and UO_2Cl_2, and then decreases in magnitude and is smallest for UO_2At_2 even though the oxyhalides from X=Br through At include the additional correlation of their d electrons. As might be expected, the effects of spin-orbit coupling are large and negative since they are mainly due to SO effects in the atoms. The effects of SO coupling in these closed-shell molecules cannot be neglected however, as can be inferred by the SO contributions shown in Table 2 for the reaction enthalpies, which range from 1.1 to 1.8 kcal/mol for Eq. (5) even though only closed-shell molecules are involved. The contributions shown in Table 1 for the Gaunt term are surprisingly large, about -8.5 kcal/mol for UF_6 and from -4.5 to -5.0 kcal/mol for UO_2X_2. The effect of the Lamb shift on the calculated atomization energies is negligible for UF_6 but ranges from 0.4 to 0.6 kcal/mol for UO_2X_2. The final calculated atomization enthalpies at 298 K are nearly within the experimental uncertainties in all 3 cases where experimental values are available. The value for UF_6 is 2.5 kcal/mol below the midpoint of the experimental value (754.7 ± 2.4 kcal/mol) while the atomization enthalpy of UO_2Cl_2 is 4 kcal/mol below experiment (536.4 ± 5.5 kcal/mol). The calculated value for UO_2F_2 is in nearly exact agreement with experiment although the latter has an uncertainty of 4.3 kcal/mol. It should be noted that all the usual coupled cluster diagnostics that might indicate multireference character are very small and similar between all the molecules of this work. Based on these results and given that the various contributions in Table 1 are all very similar, the enthalpies for the UO_2X_2 species are all expected to be accurate to about 3 kcal/mol.

In regard to the non-U-containing molecules shown in Table 1, the final results are in excellent agreement with experiment, particularly since these do not include any higher order correlation contributions beyond CCSD(T). Up through HBr, the differences between FPD and experiment is within 0.1 kcal/mol in all cases and that for HI is smaller than experiment by just 0.35 kcal/mol. The currently calculated dissociation energy for HAt shown in Table 1 is within a few tenths of a kcal/mol of values previously reported by Casetti et al. and Vasiliu et al.[64,65]

Table 2 gives the contributions to the FPD reaction enthalpies, ΔH_r, for Eqs. (5) and (6). As is usually the case, the individual contributions are much smaller compared to those of the atomization energies of Table 1 since there are significant cancellations. For the reaction involving UF_6, however, the CBS extrapolation, CV contributions, and even SO coupling are still non-negligible. It is particularly notable that in this case ΔE_{CBS} and ΔE_{CV} do not have opposite signs as in the atomization energy case, but now SO and Gaunt do. For the contributions to the enthalpy of the reaction corresponding to Eq. (6), nearly all are small with a maximum value of 1 kcal/mol, except for the contributions due to the zero-point vibrational energy which arises predominately from the difference in the ZPVEs of HF and HX.

Table 3 presents the heats of formation at 298 K as determined using the calculated atomization enthalpies or reaction enthalpy approaches. In each case, the accuracy of the final values is limited not just by the FPD approach employed but by the underlying uncertainties of the experimental formation enthalpies that were used. Specifically for the atomization energies, the heat of formation of U atom has a stated uncertainty of 1.9 kcal/mol. The experimental uncertainties for the other atoms are negligible in comparison. While the FPD formation enthalpy for UF_6 is within 2.5 kcal/mol of the accurate (±0.45 kcal/mol) experimental value, the actual error in the FPD result could in principle be over 4 kcal/mol (or only about 0.5 kcal/mol) given the uncertainty in the experimental U atom value. For the enthalpy of formation of UO_2F_2, both the atomization and reaction enthalpy approaches yield a value that is within the ±2.4 kcal/mol error bars of experiment. We adopt the average of these two results and assign a conservative uncertainty of ±4.0 kcal/mol. The current result is in close agreement with the similar FPD calculations of Bross and Peterson[22] that used Eq. (5). For UO_2Cl_2, Eq. (6) can be added to the mix but unfortunately it is also accompanied by the ±2.4 kcal/mol uncertainty in the heat of formation for UO_2F_2. For all three determinations for UO_2Cl_2, the FPD formation enthalpy is lower than the experimental result and outside of the latter's stated ±3.6 kcal/mol experimental uncertainty. Nevertheless, the average of the 3 FPD determinations is adopted with an uncertainty of ±4 kcal/mol. The same recommendation is made for X=Br and I where the experimental values are not yet known. An experimental reinvestigation of the heat of formation of UO_2Cl_2 would be very valuable. Not surprisingly, based on the atomization enthalpy results of Table 1, the FPD heats of formation for H_2O and HX (X=F-I) are in excellent agreement with experiment.

CONCLUSIONS

Atomization enthalpies and heats of formation have been calculated for UF_6 and the uranium oxyhalides UO_2X_2 with X=F, Cl, Br, I, and At using a relativistic composite approach based on CCSD(T) with extrapolations to the CBS limit. Direct calculations of the atomization energies with CCSD(T) were made possible by carrying out the calculations using the U^+ atom and utilizing the accurate experimental ionization energy of U atom. The final values agreed within the experimental uncertainties in the 3 cases in which experimental values were available, but unfortunately these uncertainties ranged from 2.4 to 5.5 kcal/mol. Based on previous investigations,[5-7,12,15] the FPD atomization enthalpies are expected to be accurate to within 3 kcal/mol. Enthalpies of formation were calculated for each species by making use of available experimental heats of formation with FPD atomization enthalpies as well as two different FPD-calculated reaction enthalpies involving UF_6, UO_2X_2, H_2O, and HX species. While the final accuracies are limited in part due to the experimental uncertainties in some of the formation enthalpies, the resulting FPD-derived values are expected to be accurate to about 4 kcal/mol.

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Table 1. Summary of contributions to the FPD atomization enthalpies at 298 K (kcal/mol).[a]

Molecule	$\Delta E_{VQZ\text{-}DK}$	ΔE_{CBS}	$\Delta E_{CV/CBS}$	ΔE_{SO}	ΔE_{Gaunt}	ΔE_{QED}	ΔE_{ZPE}	dH(298)	ΔH_{atom}	Expt.[c]
UF_6	923.04	4.89	-6.89	-14.56	-8.49	-0.03	-7.38	4.49	752.22[b]	754.7(24)
UO_2F_2	773.40	5.46	-6.64	-14.96	-4.97	0.41	-5.58	3.32	607.58[b]	607.7(43)
UO_2Cl_2	705.92	6.28	-6.67	-16.14	-4.51	0.38	-4.79	2.81	540.44[b]	536.4(55)
UO_2Br_2	681.16	6.03	-5.70	-20.93	-4.48	0.52	-4.40	2.53	511.88[b]	
UO_2I_2	651.90	5.79	-4.24	-26.84	-4.51	0.51	-4.21	2.39	477.95[b]	
UO_2At_2	637.68	5.32	-3.45	-46.41	-4.79	0.58	-4.09	2.30	444.29[b]	
H_2O	231.00	1.55	0.37	-0.22	-0.10	0.00	-13.40	2.20	221.38	221.56(1)
HF	140.73	0.78	0.18	-0.39	-0.19	0.00	-5.90	0.97	136.16	136.25(1)
HCl	106..45	0.72	0.18	-0.83	-0.03	0.00	-4.28	0.91	103.11	103.124(2)
HBr	92.38	0.56	0.50	-3.32	-0.01	0.06	-3.78	0.89	87.28	87.37(4)
HI	78.94	0.63	0.90	-6.48	0.02	0.04	-3.31	0.89	71.64	71.29(1)
HAt	71.64	0.44	1.16	-16.32	0.05	0.07	-3.06	0.89	54.86	

[a] See the text for the definition of each contribution.

[b] Includes a contribution from the experimental ionization energy of U atom, -142.84 kcal/mol. See the text.

[c] The experimental uncertainty in the last digit is given in parentheses. These values were calculated from their experimental heats of formation.[1,2,56-58]

Table 2. Summary of contributions to the FPD reaction enthalpies at 298 K (kcal/mol).

Molecule	$\Delta E_{VQZ\text{-}DK}$	ΔE_{CBS}	$\Delta E_{CV/CBS}$	ΔE_{SO}	ΔE_{Gaunt}	ΔE_{QED}	ΔE_{ZPE}	dH(298)	ΔH_r
Eq. (5) $UF_6 + 2H_2O + 2HX \rightarrow UO_2X_2 + 6HF$									
X=F	48.73	-0.58	-0.22	1.52	-2.95	-0.44	-5.02	1.72	42.75[a]
X=Cl	47.65	-1.52	-0.18	1.82	-3.09	-0.42	-2.58	2.10	43.78[b]
X=Br	44.28	-1.59	-0.51	1.63	-3.07	-0.44	-1.97	2.35	40.69
X=I	46.65	-1.20	-1.17	1.22	-3.00	-0.46	-1.21	2.49	43.33
X=At	46.27	-1.11	-1.44	1.10	-2.66	-0.48	-0.84	2.58	43.43
Eq. (6) $UO_2F_2 + 2HX \rightarrow UO_2X_2 + 2HF$									
X=Cl	-1.08	-0.93	0.04	0.30	-0.14	0.02	2.44	0.38	1.03
X=Br	-4.45	-1.00	-0.29	0.11	-0.12	0.00	3.05	0.64	-2.06
X=I	-2.08	-0.61	-0.95	-0.30	-0.04	-0.02	3.81	0.77	0.58
X=At	-2.46	-0.53	-1.21	-0.42	0.29	-0.03	4.17	0.87	0.68

[a] The experimental value calculated using the known heats of formation is 45.1 ± 2.9 kcal/mol.

[b] The experimental value calculated using the known heats of formation is 50.2 ± 4.3 kcal/mol.

Table 3. Calculated FPD heats of formation (298 K) compared to available experimental values where available (kcal/mol).

Molecule	From ΔH_{atom}[a]	Using ΔH_r of Eq. (5)[b]	Using ΔH_r of Eq. (6)[c]	Average	Expt.
UF_6	-511.03				-513.53 ± 0.45[d]
UO_2F_2	-323.12	-325.63		-324.4 ± 4.0	-323.3 ± 2.4[d]
UO_2Cl_2	-235.93	-238.29	-235.91	-236.7 ± 4.0	-231.9 ± 3.6[d]
UO_2Br_2	-211.89	-214.40	-212.03	-212.8 ± 4.0	
UO_2I_2	-180.39	-182.03	-179.65	-180.7 ± 4.0	
H_2O	-57.61				-57.792 ± 0.006[e]
HF	-65.09				-65.183 ± 0.005[e]
HCl	-22.02				-22.030 ± 0.001[e]
HBr	-8.45				-8.540 ± 0.031[e]
HI	5.98				6.326 ± 0.009[e]

[a] Results for the uranium-containing molecules include an inherent uncertainty of ±1.9 kcal/mol from the experimental uncertainty in ΔH_f(298) of U atom.[2]

[b] Results include an inherent uncertainty of ±0.45 kcal/mol from the experimental uncertainty in ΔH_f(298) of UF_6.[1]

[c] Results include an inherent uncertainty of ±2.4 kcal/mol from the experimental uncertainty in ΔH_f(298) of UO_2F_2.[1]

[d] Ref. [1]

[e] Refs. [56-58]

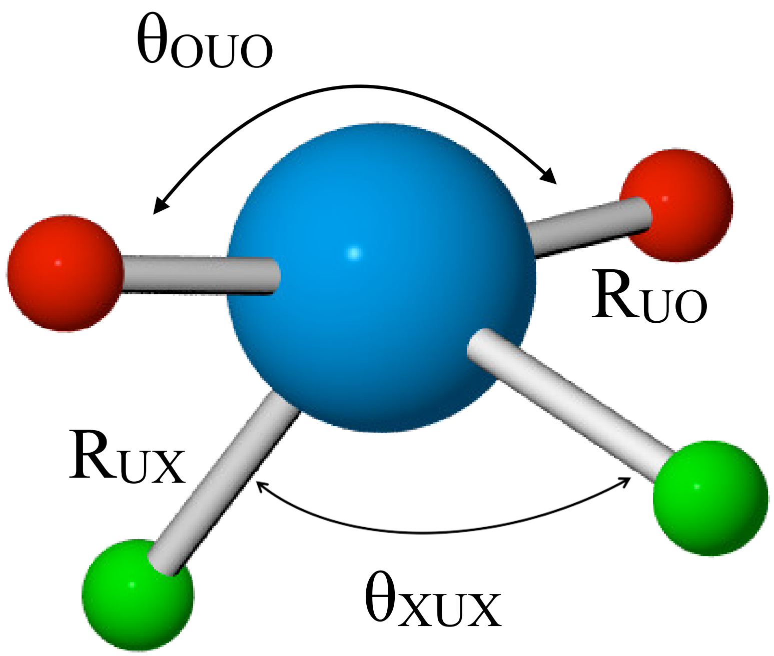
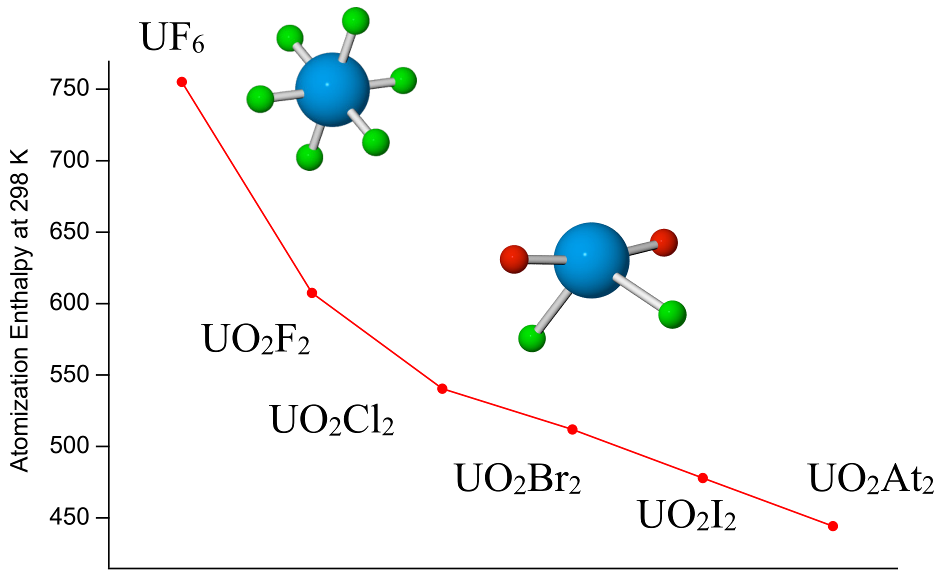


Figure 1. The general equilibrium C_{2v} structure of UO_2X_2 (X=F, Cl, Br, I, At)

TOC Graphic


UF6
UO2F2
UO2Cl2
UO2Br2
UO2I2
UO2At2
Atomization Enthalpy at 298 K
750
700
650
600
550
500
450